Crystal structure of the garnet {Mn$_3$}[Fe$_2$](Ge$_3$)O$_{12}$

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Auszug

Die Kristallstruktur des Granats {Mn$_3$}[Fe$_2$](Ge$_3$)O$_{12}$ wurde aus den mit
einem automatischen Diffraktometer gemessenen Intensitäten nach der Methode
der kleinsten Quadrate verfeinert. Der Abstand Ge—O ist mit 1,77 $\pm$ 0,02 Å um
etwa 0,03 Å größer als im Quarztyp-GeO$_2$. Das ist im Einklang mit den ent-
sprechenden Si—O-Abständen. Der Fe—O-Abstand ist 2,00 $\pm$ 0,02 Å und
stimmt mit den Abständen in drei Eisengranaten gut überein. Die Mn—O-
Abstände sind 2,30 und 2,42 $\pm$ 0,02 Å. Die Strukturergebnisse stimmen damit
überein, daß {Mn$_3$}[Fe$_2$](Ge$_3$)O$_{12}$ nicht ferrimagnetisch ist.

Abstract

The crystal structure of the garnet {Mn$_3$}[Fe$_2$](Ge$_3$)O$_{12}$ has been refined by
least-squares calculations applied to single-crystal data collected with a Buerger-
Supper-Pace-Picker automatic diffractometer. The Ge—O distance is 1.77
$\pm$ 0.02 Å (limits of error), about 0.03 Å longer than the Ge—O distance in
quartz-type GeO$_2$. This is in accord with the analogous Si—O distances. The
Fe—O distance is 2.00 $\pm$ 0.02 Å in good agreement with the analogous distance
in three iron garnets. The Mn—O distances are 2.30 and 2.42 $\pm$ 0.02 Å. The
structural results are in accord with the absence of ferrimagnetism in the
{Mn$_3$}[Fe$_2$](Ge$_3$)O$_{12}$ garnet.

Introduction

A recent paper[1] reviews the results of garnet structure[2] refinements
reported to about mid-1967. These include results on Y$_3$Fe$_2$Fe$_3$O$_{12}$
and on other rare-earth iron, gallium, and aluminum garnets as well
as on some silicate garnets. In this paper we report the results of the

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[1] S. Geller, Crystal chemistry of the garnets. Z. Kristallogr. **125** (1967)
1—47.

[2] G. Menzer, Die Kristallstruktur von Granat. Centralbl. Min. [A] **1925**,
344—345; Z. Kristallogr. **63** (1926) 157—158; Die Kristallstruktur der Gra-
nate. Z. Kristallogr. **69** (1928) 300—396.

refinement of the structure of manganese iron germanate, $\{Mn_3\}[Fe_2](Ge_3)O_{12}$, garnet. This serves four purposes: (1) it is the first garnet refinement which gives a comparison of the tetrahedral Ge^{4+}—O^{2-} distance with that of quartz-type GeO_2; (2) it is the first accurate determination of the 8-coordination distances of Mn^{2+} ion in a garnet; (3) it gives another octahedrally coordinated Fe^{3+}—O^{2-} distance to compare with the many measured in other garnets; (4) it gives further insight into the magnetic behavior of this garnet.

The first synthesis of $Mn_3Fe_2Ge_3O_{12}$ was made by TAUBER, BANKS and KEDESDY[3] and confirmed by GELLER, MILLER and TREUTING[4], who also reported obtaining single crystals of this garnet from reaction mixtures which had been carried to the melting point of about 1235 to 1240°C. A crystal obtained from the work done almost ten years ago has been used for the present refinement.

Susceptibility vs temperature measurements made on this garnet indicated the occurrence of an antiferromagnetic transition at 6°K[5]. The low Néel temperature indicates that the magnetic interactions within the Mn^{2+} and within the Fe^{3+} sublattices are very weak. If ordering of moments occurs in both, each sublattice is antiferromagnetic, and it is probable that the two are not colinear. The results of the structure refinement are in accord with the absence of ferrimagnetism in this garnet.

Crystal data

Crystals of $\{Mn_3\}[Fe_2](Ge_3)O_{12}$ are cubic, $a = 12.087 \pm 0.003$ Å, most probable space group $Ia3d$—O_h^{10}. The unit cell with volume 1765.9 Å^3 contains eight $Mn_3Fe_2Ge_3O_{12}$ with formula weight 686.27. The calculated density $\varrho_x = 5.162$ g cm^{-3}. The linear absorption coefficient for $MoK\alpha$ radiation is 180 cm^{-1}.

Experimental

A Buerger-Supper-Pace-Picker automatic diffractometer was used to collect the data, obtained with $MoK\alpha$ radiation and balanced Zr and Y filters from a spherical crystal, of 0.134 mm radius, prepared in

[3] A. TAUBER, E. BANKS and H. KEDESDY, Magnetic germanates isostructural with garnet. J. Appl. Physics 29 (1958) 385—387.

[4] S. GELLER, C. E. MILLER and R. G. TREUTING, New synthetic garnets. Acta Crystallogr. 13 (1960) 179—186.

[5] R. M. BOZORTH and S. GELLER, Interactions and distributions of magnetic ions in some garnet systems. J. Physics Chem. Solids 11 (1959) 263—267.

a Bond sphere grinder[6]. Intensities of reflections with h, k, l all positive and for $2\theta \leqq 50°$ were measured. The continuous scan mode was used: scan rate $= 1.00°/min$, scan interval $= 2.00°$. A sixty-second background count was taken at the beginning and the end of the scan interval. Absorption corrections[7] and Lorentz-polarization-Tunell factors were applied to the intensities. A total of 136 independent structure amplitudes was obtained; most were the averages of values measured for from three to six equivalent reflections.

Refinement of structural parameters

The cations Mn^{2+}, Fe^{3+} and Ge^{4+} are in the special positions $24c$, $16a$ and $24d$, respectively, of space group $Ia3d$. The oxygen ions are in the general positions $96h$. Therefore, the variables in the problem are the oxygen-ion positions and thermal parameters, the cation thermal parameters, and a scale factor to put the observed structure amplitudes on an absolute scale. The parameters of synthetic pyrope, reported by GIBBS and SMITH[8], were used as the trial parameters in the least-squares calculations. The scattering factors used were: for O^{2-}, those given by TOKONAMI[9]; for Mn^{2+} and Fe^{3+}, those given by CROMER and WABER[10]; and for Ge^{4+}, those given by PIPER[11]. For the cations the anomalous dispersion corrections (both real and imaginary parts) given by CROMER[12] were applied.

For refining the oxygen ion parameters, only the following classes of data, to which the cation contribution is zero or small, were used: (I) For hkl with two indices odd and the third divisible by 4, for $hk0$ with h (or k) $= 8n$ and k (or h) $= 2m$, n and m odd, and for the reflections 2, 4, 12 and 4, 6, 12, the cation contribution is zero and the

[6] W. L. BOND, Making small spheres. Rev. Sci. Instr. 22 (1951) 344.

[7] W. L. BOND, Weissenberg intensity correction factors for absorption in spheres and cylinders, and for monochromatized radiation. Acta Crystallogr. 12 (1959) 375—381.

[8] G. V. GIBBS and J. V. SMITH, Refinement of the crystal structure of synthetic pyrope. Amer. Mineral 50 (1965) 2023—2039.

[9] M. TOKONAMI, Atomic scattering factor for O^{2-}. Acta Crystallogr. 19 (1965) 486.

[10] D. T. CROMER and J. T. WABER, Scattering factors computed from relativistic Dirac-Slater wave functions. Acta Crystallogr. 18 (1965) 104—109.

[11] W. W. PIPER, unpublished work, tabulated by J. A. IBERS in International tables for x-ray crystallography, Vol. III, Birmingham, Kynoch Press (1962).

[12] D. T. CROMER, Anomalous dispersion corrections computed from self-consistent field relativistic Dirac-Slater wave functions. Acta Crystallogr. 18 (1965) 17—23.

data depend only on the oxygen-ion parameters. (II) For hkl with two indices odd and the third equal $2n$, n odd, the total cation contribution is of the form $\pm 8\,(f^{\mathrm{T}}_{\mathrm{Mn}^{2+}} - f^{\mathrm{T}}_{\mathrm{Ge}^{4+}})\,\sin\frac{1}{4}\pi h$, where $f^{\mathrm{T}}_{\mathrm{Mn}^{2+}}$ and $f^{\mathrm{T}}_{\mathrm{Ge}^{4+}}$ are the room-temperature scattering factors of the Mn^{2+} and Ge^{4+} ions, respectively. A total of 96 independent data belong to these two classes. The remainder of the data, which in general have large contributions from the cations, were found to be substantially affected by extinction and were therefore omitted from the calculations.

Two series of least-squares calculations[13], one using the data of both classes I and II and the other using only those of class I, were carried out. The two refinements converged quickly to final parameter values which differ slightly but not significantly. Because there seems to be no real basis for deciding between the two sets of final parameter values, both, together with the averages, are given in Table 1.

Table 1. *Oxygen-ion parameters*

(Standard deviations are in parentheses)

Parameter	(1) Based on data of Class I	(2) Based on data of Classes I and II	(3) Average
x	0.02997 (0.00025)	0.02982 (0.00038)	0.02990
y	0.05453 (0.00029)	0.05331 (0.00039)	0.05392
z	0.65305 (0.00034)	0.65317 (0.00037)	0.65311
β_{11}	0.00177 (0.00026)	0.00174 (0.00031)	0.00176
β_{22}	0.00054 (0.00026)	0.00143 (0.00035)	0.00099
β_{33}	0.00105 (0.00027)	0.00122 (0.00034)	0.00114
β_{12}	-0.00011 (0.00024)	0.00028 (0.00028)	0.00009
β_{13}	0.00007 (0.00027)	-0.00032 (0.00023)	-0.00012
β_{23}	-0.00075 (0.00021)	-0.00015 (0.00024)	-0.00045

The data used did not permit refinement of the cation thermal parameters[14]. Therefore, for the cations, isotropic thermal parameters, $B_{\mathrm{Mn}} = 0.25$ Å² and $B_{\mathrm{Ge}} = 0.19$ Å², were estimated from the oxygen-ion thermal parameters by assuming these parameters to be related inversely as the atomic weights. These were kept constant throughout

[13] W. R. BUSING, K. O. MARTIN and H. A. LEVY, ORFLS, a FORTRAN crystallographic least-squares program. ORNL-TM-305 (1962), with modifications by J. A. IBERS, W. C. HAMILTON, C. K. JOHNSON, R. D. ELLISON and H. A. LEVY.

[14] S. GELLER, Parameter interaction in least-squares structure refinement. Acta Crystallogr. 14 (1961) 1026–1035.

the calculations. It is unlikely that the oxygen-ion positional parameters are affected by this treatment because (1) the thermal parameters are small, (2) there are no large correlations[14] between the thermal parameters and the oxygen-ion positional parameters, and (3) the results of the two refinements agree well.

After the refinement had converged, additional iterations were carried out with the Ge^{4+} multiplier as a variable; there was no indication of a distribution of the Fe^{3+} and Ge^{4+} ions over both the octahedral and tetrahedral sites. On the contrary, the multiplier increased by 3.2%, which indicates that the Ge^{4+} form factors are somewhat in error or, perhaps, that in this case, form factors for Ge^{3+} should be used. This was not pursued further, however.

Table 2. *Observed and calculated structure amplitudes*

h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$
0	2	8	68	68	1	7	8	21	24	2	5	5	<10	13	3	5	8	82	89	4	6	12	<13	13
0	6	8	14	13	1	6	9	35	37	2	3	7	105	105	3	4	9	47	46	5	5	6	12	10
0	8	10	24	20	1	2	11	28	21	2	5	7	93	88	3	3	10	14	19	5	6	7	11	9
1	1	2	49	54	1	5	10	18	17	2	3	9	33	34	3	7	8	15	19	5	7	8	13	12
1	2	3	78	77	1	4	11	35	35	2	7	7	26	25	3	6	9	43	39	5	6	9	34	32
1	3	4	113	119	1	8	9	46	48	2	5	9	53	48	3	5	10	36	36	5	5	10	54	55
1	2	5	45	56	1	7	10	11	13	2	3	11	52	45	3	4	11	22	25	5	8	9	24	25
1	1	6	92	97	1	3	12	37	40	2	7	9	74	68	3	8	9	13	14	5	7	10	56	48
1	4	5	25	27	1	6	11	51	42	2	3	11	51	44	3	7	10	33	30	5	6	11	39	30
1	5	6	84	85	1	5	12	<13	8	2	4	12	<13	3	3	6	11	17	20	5	9	10	60	57
1	2	7	50	47	1	2	13	78	73	2	9	9	<13	9	3	5	12	36	36	6	7	7	86	80
1	5	6	46	44	1	9	10	38	32	2	7	11	24	19	3	9	10	52	55	6	7	9	<12	9
1	4	7	56	59	1	4	13	<13	5	2	3	13	29	25	3	4	13	23	24	6	9	9	97	96
1	3	8	20	21	1	8	11	19	17	2	5	13	85	80	3	8	11	<13	12	6	7	11	48	42
1	2	9	58	53	1	7	12	<13	2	2	9	11	29	26	3	7	12	45	43	7	8	9	24	22
1	6	7	116	114	1	1	14	35	36	3	4	5	16	15	4	5	7	73	75	7	7	10	57	56
1	5	8	61	62	1	3	14	16	12	3	3	6	46	49	4	5	9	<12	0					
1	4	9	69	73	1	6	13	45	44	3	5	6	102	100	4	7	9	16	15					
1	1	10	104	103	2	3	3	214	233	3	4	7	39	41	4	5	11	<13	3					
1	3	10	48	52	2	3	5	27	31	3	6	7	47	47	4	7	11	47	50					

Table 2 compares the observed structure amplitudes with those calculated from the final average parameter values [column (3) of Table 1]. For the complete set of data in Table 2, the conventional

$$R = \frac{\Sigma ||F_o| - |F_c||}{\Sigma |F_o|} = 0.070.$$ For the data of class I only, $R = 0.055$.

Interionic distances and angles

Interionic distances and angles, computed from the final average parameter values [column (3) of Table 1], are given in Table 3. The standard errors given in Table 3 are based on the larger standard deviations, those in column (2) of Table 1. The *limits of error* are taken as three times the standard errors.

Discussion

The refinement of the structure of $Mn_3Fe_2Ge_3O_{12}$ gives the first determination of the tetrahedral Ge^{4+}—O^{2-} and 8-coordination Mn^{2+}—O^{2-} distances in a garnet. The Ge^{4+}—O^{2-} distance, 1.766 Å, is significantly longer than the Ge^{4+}—O^{2-} distances, 1.737 and 1.741 Å, in quartz-type GeO_2[15]. The difference is about the same as occurs in the analogous Si^{4+}—O^{2-} distances[1], indicating perhaps more ionicity in these bonds in the garnets than in the quartz-type structures. The two Mn^{2+}—O^{2-} distances are 2.30 and 2.42 Å. These are rather close

Table 3. *Interatomic distances and angles*

GeO₄ tetrahedron	Ge—O	(4) 1.766Å (0.007Å)*
	O—O	(2) 2.681Å (0.013Å), (4) 2.980Å (0.013Å)
	O—Ge—O	(2) 98.8° (0.5°), (4) 115.1° (0.3°)
FeO₆ octahedron	Fe—O	(6) 1.995Å (0.007Å)
	O—O	(6) 2.712Å (0.012Å), (6) 2.926Å (0.014Å)
	O—Fe—O	(6) 85.7° (0.1°), (6) 94.3° (0.3°)
MnO₈ dodecahedron	Mn—O	(4) 2.303Å (0.007Å), (4) 2.421Å (0.007Å)
(distorted cube)	O—O**	(2) 2.681Å (0.013Å), (4) 2.712Å (0.012Å),
		(4) 2.766Å (0.017Å), (2) 2.921Å (0.016Å),
		(4) 3.484Å (0.004Å), (1) 3.816Å (0.012Å),
		(1) 3.922Å (0.015Å),
	O—Mn—O	(4) 70.0° (0.4°), (2) 71.2° (0.4°),
		(4) 71.6° (0.4°), (2) 74.2° (0.3°)
	Mn—Fe	(4) 3.378Å
	Mn—Ge	(2) 3.022Å, (4) 3.701Å
	Fe—Ge	(6) 3.378Å
	Fe—O—Ge	(6) 127.8° (0.9°)
	Fe—O—Mn	(6) 99.4° (0.4°), (6) 103.4° (0.5°)
	Ge—O—Mn	(4) 95.0° (0.4°), (4) 123.5° (0.7°)
	Mn—O—Mn	(8) 103.1° (0.5°)

* (frequency of occurrence) distance or angle (standard error).

** These are the *edges* of the dodecahedron. The last three independent O—O distances are the diagonal *edges* of the "twisted cube". These are six other diagonals (not edges of the dodecahedron): (1) 3.816 Å (0.012 Å), (1) 3.922 Å (0.015 Å), (4) 4.185 Å (0.004 Å). In Ref.[16], Table 3, the distance taken for the 4-multiple diagonal edge should have been 3.45 Å instead of 4.24 Å.

[15] G. S. SMITH and P. B. ISAACS. The crystal structure of quartz-like GeO_2. Acta Crystallogr. **17** (1964) 842—6.

[16] S. C. ABRAHAMS and S. GELLER. Refinement of the structure of a grossularite garnet. Acta Crystallogr. **11** (1958) 437—441.

[17] S. GELLER and M. A. GILLEO. Crystal structure and ferrimagnetism of yttrium iron garnet. J. Physics Chem. Solids **3** (1957) 30—36. (See also Structure Reports **21**, pp. 294—297).

to the Y^{3+}—O^{2-} distances, 2.37 and 2.43 Å in yttrium-iron garnet[17]. The averages are 2.36 and 2.40 Å, respectively. The Ca^{2+}—O^{2-} distances in grossularite[16,18] are 2.33 and 2.49 Å, average, 2.41 Å, again quite close to the value for the average Mn^{2+}—O^{2-} distance. There appears to be an anomaly here, but it more likely involves the Ca^{2+}—O^{2-} distances than the others. The coordination-number-6 distances from NaCl type structures of CaO[19] and MnO[20] are 2.40 and 2.22 Å, respectively, while the average CN 6 Y^{3+}—O^{2-} distance[21] is 2.28 Å. Examination of the differences for CN 6 distances indicates that the CN 8 average distances of Mn^{2+}—O^{2-} and Y^{3+}—O^{2-} are nominally in *relative* agreement with the CN 6 distances. On the other hand, the Ca^{2+} ion seems to be "contracted" in the grossularite garnet. Further structure refinements of garnets with c sites filled with Mn^{2+} or Ca^{2+} ions should be of interest in this regard.

The Fe^{3+}—O^{2-} distance, 2.00 Å, agrees well with the octahedral Fe^{3+}—O^{2-} distance found in yttrium-iron garnet by GELLER and GILLEO[17] and by BATT and POST[22], in gadolinium-iron garnet by WEIDENBORNER[23], and in ytterbium-iron garnet by EULER and BRUCE[24]. The octahedral Fe^{3+}—O^{2-} distances reported for other iron garnets including that of yttrium by EULER and BRUCE[24] are higher, but do not show a trend with size of rare earth. While it might be argued that the error limits make the differences of questionable significance, the refinements of several different garnet structures with octahedral Fe^{3+} distances should show a trend of some reasonable sort. Because the agreement with a value of 2.00—2.01 Å found for such a variety of garnets (i.e., YFe, GdFe and YbFe garnets and

[18] W. PRANDL, Verfeinerung der Kristallstruktur des Grossulars mit Neutronen- und Röntgenstrahlbeugung. Z. Kristallogr. 123 (1966) 81—116.

[19] L. OFTEDAL, Die Gitterkonstanten von CaO, CaS, CaSe, CaTe. Z. physik. Chem. 128 (1927) 154—158.

[20] See J. D. H. DONNAY, G. DONNAY, E. G. COX, O. KENNARD and M. V. KING, Crystal Data, Determinative Tables, Second Edition, A.C.A. (1963) for the many references to MnO.

[21] M. G. PATON and E. N. MASLEN, A refinement of the crystal structure of yttria. Acta Crystallogr. 19 (1965) 307—310. — A. FERT, Structure of some rare earths. Bull. Soc. franç. Mineral. Cristallogr. 85 (1962) 267—270.

[22] A. BATT and B. POST, A procedure for parameter refinement in simple structures. Acta Crystallogr. 15 (1962) 1268—1270.

[23] J. WEIDENBORNER, Least-squares refinement of the structure of gadolinium-iron garnet, Gd3Fe2Fe3O12. Acta Crystallogr. 14 (1961) 1051—1056.

[24] F. EULER and J. A. BRUCE, Oxygen coordinates of compounds with garnet structure. Acta Crystallogr. 19 (1965) 971—978.

$Mn_3Fe_2Ge_3O_{12}$) is already so good, it would seem that some of the iron-garnet structures refined by EULER and BRUCE[24] warrant restudy.

The departures from regularity of the three coordination polyhedra in $Mn_3Fe_2Ge_3O_{12}$ are similar to those found in other garnets. The GeO_4 tetrahedra are elongated in the directions parallel to the $\bar{4}$ axes as are the corresponding tetrahedra in all other garnets for which accurate structural data are available[1,8,16-18,22-25]. The FeO_6 octahedra are elongated in the directions parallel to the $\bar{3}$ axes as are the corresponding octahedra in all established cases except that of grossularite[1,8,16-18,22-26]. The shorter edges of the tetrahedra and the octahedra (2.681 and 2.712 Å) are shared with the MnO_8 dodecahedra and are also the shortest edges of the latter. The next-longest edge of the dodecahedron (2.766 Å) is shared with another dodecahedron.

In an earlier paper[5], it was indicated that there were several possible reasons for the absence of ferrimagnetism in $Mn_3Fe_2Ge_3O_{12}$: (1) weak interaction because of unfavorable geometry, (2) distribution of Fe^{3+} ions over the octahedral and tetrahedral sites resulting in a marked weakening of interaction, and (3) inherently weak interaction between Mn^{2+} and Fe^{3+} ions. Ferrimagnetism had been observed in $\{Gd_3\}[Mn_2](GaGe_2)O_{12}$[27] and since it was expected that a Gd^{3+}-O^{2-}-Mn^{2+} interaction should be weaker than a Mn^{2+}-O^{2-}-Fe^{3+} interaction, the third possibility was assumed to be unlikely. The second possibility is ruled out by the present analysis.

The Mn^{2+}—O^{2-}—Fe^{3+} angles in $Mn_3Fe_2Ge_3O_{12}$ (Table 3) appear to be unfavorable[28] for interaction; for comparison the Me(a)—O—Me(d) angle[29] in $MnFe_2O_4$ is 123°. Furthermore in this almost normal ferrospinel, the Me(a)—O distance is 1.95 Å, while in the garnet the Mn—O distances 2.30 and 2.42 Å are considerably longer. (Of course, the longer distances in the garnet are to be expected because of the higher coordination of Mn^{2+} ions, i.e., eight in the garnet as against four in the spinel.) The first possibility would then appear to be the most likely.

[25] J. ZEMANN, Zur Kristallchemie der Granate. Beitr. Mineralogie Petrographie 8 (1962) 180—188.

[26] In Ref.[1] the word "longer" in the eleventh line of Page 9 should be replaced by the word "shorter".

[27] M. A. GILLEO and S. GELLER, The interaction of magnetic ions in $Gd_3Mn_2Ge_2GaO_{12}$ and related garnets. J. Physics Chem. Solids 10 (1959) 187—190.

[28] P. W. ANDERSON in Magnetism, edited by G. T. RADO and H. SUHL, Vol. 1, pp. 25—83 (Academic Press, New York, 1963).

[29] J. M. HASTINGS and L. M. CORLISS, Neutron diffraction study of manganese ferrite. Physic. Rev. 104 (1956) 328—331.